JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. HEI 9[1997]-255713

Int. Cl.[6]:	C 08 F 4/80 10/00
Filing No.:	Hei 8[1996]-70333
Filing Date:	March 26, 1996
Publication Date:	September 30, 1997
No. of Claims:	1 (Total of 12 pages; OL)
Examination Request:	Not filed

POLYMERIZATION METHOD OF OLEFIN

Inventor: Tomohiro Yorisue
Asahi Chemical Industry Co., Ltd.
3-13-1 Shiodori, Kurashiki-shi,
Okayama-ken

Applicant: 000000033
Asahi Chemical Industry Co., Ltd.
1-2-6 Dojimahama, Kita-ku, Osaka-shi, Osaka-fu, 530 Japan

[There are no amendments to this patent.]

Abstract

Purpose

To provide a method for manufacturing an olefin polymer with a branched structure and a narrow molecular weight distribution or an olefin copolymer with a branched structure and a narrow molecular weight distribution and a narrow composition distribution, with excellent polymer yield per unit weight of catalyst.

Constitution

A polymerization method of olefin using a catalyst made of a compound of a group 10 transition metal element represented by general formula LMX_2, such as 1,1'-bis(diphenylphosphino)ferrocene nickel dichloride or the like. In the general formula, L represents a prescribed bidentate chelating ligand; X represents hydrogen or a monovalent ligand selected from groups bonded with M by means of elements from groups 14-17 of the periodic table; and M represents a transition metal element selected from group 10 of the periodic table.

Claim

A polymerization method of olefin characterized by the fact that it makes use of a catalyst made of a transition metal element selected from group 10 of the periodic table represented by the following general formula (I):

$$LMX_2 \qquad (I)$$

here in general formula (I), L, M, X are defined as follows:

L: bidentate chelating ligand represented by following general formula (II):

$$A_1-Y-A_2 \qquad (II)$$

A_1, A_2: monodentate group coordinated to M by an element selected from group 15 of the periodic table;

Y: group for connecting A_1 and A_2 with a covalent bond and selected from hydrocarbon groups and groups containing elements from groups 8, 14-16 of the periodic table;

X: hydrogen atom or monovalent ligand selected from the group bonded with M by elements from groups 14-17 of the periodic table;

M: transition metal element selected from the elements from group 10 of the periodic table.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to a polymerization method of olefin. More specifically, the present invention pertains to a method for manufacturing an olefin polymer with a branched structure and a narrow molecular weight distribution or an olefin copolymer with a branched structure and a narrow molecular weight distribution and a narrow composition distribution, with excellent polymer yield per unit weight of catalyst.

[0002]

Prior art

It is well known that the compounds of elements from group 10 of the periodic table, especially the Ni compounds, can be used as effective catalysts for low polymerization of olefin (for example, see the following reference: The Organic Chemistry of Nickel, Vol. II, Chapter 1 (1975)).

[0003]

On the other hand, various tests have been performed to obtain high olefin polymers by means of control of the ligand contained in the compounds of elements from group 10 of the periodic table. For example, the following methods have been developed: a method of polymerization of carboxyphosphine, benzoylphosphine, phenoxyphosphine, etc., by means of a compound coordinated to Ni (see: J. Mol. Cat., Vol. 41, p. 123, 1987; Angew. Chem., Int. Ed. Engl., Vol. 26, p. 63, 1987; Organometallics, Vol. 2, p. 594, 1983; Japanese Kokai Patent Application Nos. Hei 3[1991]-131608, Hei 3[1991]-131611, etc.), a method of polymerization of aminobis(imino) phosphine by means of a compound coordinated to Ni (see: Angew Chem., Int. Ed. Engl., Vol. 20, p. 116, 1981, ibid., Vol. 24, p. 1001, 1985; Japanese Kokai Patent Application Nos. Sho 61[1986]-228003, Hei 3[1991]-115311, Hei 3[1991]-206607, Hei 3[1991]-261809, Hei 3[1991]-277610, EPO 38495/90, etc.); a method of polymerization of diazabutadiene using a compound coordinated to Ni or Pd, methyl aluminoxane, or ion pair type compound having non-coordinated anion (see: J. Am. Chem. Soc., Vol. 117, p. 6414, 1995; ibid., Vol. 118, p. 267, 1996).

[0004]

However, all of the aforementioned methods have the disadvantage that the molecular weight of the obtained olefin polymer is still low.

[0005]

Problems to be solved by the invention

The purpose of the present invention is to solve the aforementioned problems of the prior art by providing a method for manufacturing an olefin polymer with a branched structure and a narrow molecular weight distribution or an olefin copolymer with a branched structure and a narrow molecular weight distribution and a narrow composition distribution, with excellent polymer yield per unit weight of catalyst.

[0006]

Means to solve the problems

In order to solve the aforementioned problems, the present inventors have performed extensive research. As a result of this research, it was found that the compound of elements from group 10 of the periodic table represented by the following general formula (I) is effective in the polymerization of phosphine. As a result, the present invention was reached. That is, the present invention provides a polymerization method of olefin characterized by the fact that it makes use of a catalyst made of a transition metal element selected from group 10 of the periodic table represented by following general formula (I):

[0007]

$$LMX_2 \qquad (I)$$

here in general formula (I), L, M, X are defined as follows:

L: bidentate chelating ligand represented by following general formula (II):

$$A_1-Y-A_2 \qquad (II)$$

A_1, A_2: monodentate group coordinated to M by an element selected from group 15 of the periodic table;

Y: group for connecting A_1 and A_2 with a covalent bond and selected from hydrocarbon groups and groups containing elements from groups 8, 14-16 of the periodic table;

X: hydrogen atom or monovalent ligand selected from the group bonded with M by elements from groups 14-17 of the periodic table;

M: transition metal element selected from the elements from group 10 of the periodic table.

[0008]

In the following, an explanation will be given in more detail regarding the present invention. In general formula (I), L represents a bidentate chelating ligand coordinated to M by means of an element selected from group 15 of the periodic table and represented by general formula (II). In general formula (II), A_1, A_2 represent monodentate groups coordinated to M by an element selected from group 15 of the periodic table, such as groups coordinated by nitrogen atoms, such as an amino group, amino group/imino group having 1-2 substituents, imino group having 1 substituent, etc.; groups coordinated by phosphorus atoms, such as a phosphine group, phosphine group having 1-2 substituents, phospheno group, phospheno group having 1 substituent, etc.; groups coordinated by arsenic atoms, such as arsino group, arsino group having 1-2 substituents, etc.; groups coordinated by antimony atoms, such as stibino group, stibino group having 1-2 substituents, etc. Examples of substituents include methyl group, ethyl group,

n-propyl group, isopropyl group, n-butyl group, isobutyl group, t-butyl group, and other C_{1-20} alkyl groups; cyclopentyl group, cyclohexyl group, and other C_{3-8} cycloalkyl groups; phenyl group, o-tolyl group, p-tolyl group, mesityl group, 2,4,6-tri-t-butylphenyl group, and other C_{6-30} alkylaryl groups; benzyl group and other C_{7-20} arylalkyl groups; hydroxyethyl group, p-hydroxyphenyl group, and other C_{1-20} hydroxyl group-substituted hydrocarbon groups; methoxyethyl group, p-methoxyphenyl group, and other C_{1-20} oxygen-containing hydrocarbon group-substituted C_{1-20} hydrocarbon groups; aminoethyl group, p-aminophenyl group, and other amino group-substituted C_{1-20} hydrocarbon groups, dimethylamino ethyl group, p-dimethylaminophenyl group, and other C_{1-20} hydrocarbon groups substituted with C_{1-20} nitrogen-containing hydrocarbon groups; trifluoromethyl group, p-fluorophenyl group, penta-fluorophenyl group, and other C_{1-20} halogen-substituted hydrocarbon groups; trimethylsilyl group, tributylsilyl group, and other silyl groups substituted with C_{1-20} hydrocarbon groups; amino group, dimethylamino group, diethylamino group, diphenylamino group, and other amino groups substituted with C_{1-20} hydrocarbon groups; hydroxyl group, methoxy group, ethoxy group, butoxy group, and other C_{1-20} alkoxy groups; phenoxy group, o-tolyloxy group, p-tolyloxy group, and other C_{6-20} alkylaryloxy groups; benzyloxy group and other C_{7-20} arylalkyloxy groups; fluorine, chlorine, bromine, iodine, and other halogen atoms; etc. When there are multiple said substituents, they may be bonded to each other by a covalent bond. A_1 and A_2 may be identical to each other or different from each other. The preferable examples of the combinations for A_1 and A_2 include the combination of groups both coordinated by phosphorus atoms, the combination of the group coordinated by a phosphorus atom and the group coordinated by a nitrogen atom, etc.

[0009]

Examples of the groups that can be used as Y include the groups selected from hydrocarbon groups and the groups containing elements from groups 8, 14-16 of the periodic table with the two terminal atoms connected to A_1 and A_2 by means of covalent bonds with A_1 and A_2. Specific examples include hydrocarbon groups, such as methylene group, ethylene group, trimethylene group, tetramethylene group, and other C_{1-6} straight-chain alkylene groups, methylmethylene group, methylethylene group, dimethylethylene group, phenylethylene group, and other C_{1-6} straight-chain alkylene groups substituted by C_{1-20} hydrocarbon substituents, cyclopentalene group, cyclohexylene group, norbornylene group, and other C_{3-10} cyclic alkylene groups, methyl cyclopentalene group, methyl cyclohexylene group, dimethyl cyclohexylene group, and other C_{3-10} cyclic alkylene groups substituted with C_{1-20} hydrocarbon groups, methyl methine group, phenyl methine group, and other C_{1-4} alkyne groups substituted by C_{1-20} hydrocarbon substituents, ethylidene group, and other C_{2-6} straight-chain alkenylene groups, dimethyl ethylidene group, diphenyl ethylidene group, and other C_{2-6} straight-chain

alkenylene groups substituted by C_{1-20} hydrocarbon substituents, cyclopentelene [transliteration] group, cyclohexelene group, and other C_{3-10} cyclic alkenylene groups, methyl cyclopentelene group, methyl cyclohexelene group, and other C_{3-10} cyclic alkenylene groups substituted by C_{1-20} hydrocarbon substituents, butadienylene group, hexadienylene group, and other C_{4-8} straight-chain alkadienylene groups, methyl butadienylene group, dimethyl butadienylene group, and other C_{4-8} alkadienylene groups substituted by C_{1-20} hydrocarbon substituents, cyclopentadienylene group, and other C_{4-10} cyclic alkadienylene groups, methyl cyclopentadienylene group, and other C_{5-10} cyclic alkadienylene groups substituted by C_{1-20} hydrocarbon substituents, phenylene group, 1,1'-biphenylene group, 1,1'-binaphthyl group, and other C_{6-30} arylene groups, 6,6'-dimethyl-1,1'-biphenylene group, and other C_{6-30} arylene groups substituted by C_{1-20} hydrocarbon substituents, benzerene [transliteration] and other C_{7-20} arylene alkarene [transliteration] groups benzyline group, and other C_{7-20} arylene alkyne groups, etc. Examples of the groups containing elements from group 8 of the periodic table include groups containing iron atoms, such as ferrocenylene, methyl ferrocenylene group, dimethyl ferrorcenylene group, and other ferrocenylene groups substituted by C_{1-20} hydrocarbon substituents. Examples of the groups containing ruthenium atoms include ruthenocenylene group, methyl ruthenocenylene group, dimethyl ruthenocenylene group, and other ruthenocenylene groups substituted by C_{1-20} hydrocarbon substituents. Examples of the groups containing osmium atoms include osmocenylene group, methyl osmocenylene group, dimethyl osmocenylene group, and other osmocenylene groups substituted by C_{1-20} hydrocarbon substituents, etc.

[0010]

The groups containing elements from groups 14-16 of the periodic table are groups represented by the following general formulas (III) and (IV).

$$-Z_1-B- \qquad (III)$$

$$-Z_1-B-Z_2- \qquad (IV)$$

where, Z_1, Z_2, B have the following meanings.

Z_1, Z_2: hydrocarbon groups;

B: divalent group bonded by element selected from the elements from groups 14-16 of the periodic table

[0011]

Examples of the hydrocarbon groups that can be used as Z_1 and Z_2 include methylene group, ethylene group, trimethylene group, tetramethylene group, and other C_{1-6} straight-chain alkylene groups, methyl methylene group, methyl ethylene group, dimethyl ethylene group,

phenyl ethylene group, and other C1-6 straight-chain alkylene groups substituted by C1-20 hydrocarbon substituents, cyclopentalene group, cyclohexylene group, norbornylene group, and other C_{3-10} cyclic alkylene groups, methyl cyclopentalene group, methyl cyclohexylene group, dimethyl cyclohexylene group, and other C_{3-10} cyclic alkylene groups substituted with C_{1-20} hydrocarbon groups, methyl methine group, phenyl methine group, and other C_{1-4} alkyne groups substituted by C_{1-20} hydrocarbon substituents, ethylidene group, and other C_{2-6} straight-chain alkenylene groups, dimethyl ethylidene group, diphenyl ethylidene group, and other C_{2-6} straight-chain alkenylene groups substituted by C_{1-20} hydrocarbon substituents, cyclopentelene group, cyclohexelene group, and other C_{3-10} cyclic alkenylene groups, methyl cyclopentelene group, methyl cyclohexelene group, and other C_{3-10} cyclic alkenylene groups substituted by C_{1-20} hydrocarbon substituents, butadienylene group, hexadienylene group, and other C_{4-8} straight-chain alkadienylene groups, methyl butadienylene group, dimethyl butadienylene group, and other C_{4-8} alkadienylene groups substituted by C_{1-20} hydrocarbon substituents, cyclopentadienylene group, and other C_{4-10} cyclic alkadienylene groups, methyl cyclopentadienylene group, and other C_{5-10} cyclic alkadienylene groups substituted by C_{1-20} hydrocarbon substituents, phenylene group, 1,1'-biphenylene group, 1,1'-binaphthyl group, and other C_{6-30} arylene groups, 6,6'-dimethyl-1,1'-biphenylene group, and other C_{6-30} arylene groups substituted by C_{1-20} hydrocarbon substituents, benzerene and other C_{7-20} arylene alkarene groups, benzyline group, and other C_{7-20} arylene alkyne groups, etc. Here, Z_1 and Z_2 may be identical to each other or different from each other.

[0012]

Examples of the divalent groups B bonded by the elements from groups 14-16 of the periodic table include groups bonded by silicon atoms, such as silirene [transliteration] group, methyl silirene group, dimethyl silirene group, and other silirene groups substituted by C_{1-20} hydrocarbon substituents, groups bonded by germanium atoms, such as germirene [transliteration] group, methyl germirene group, dimethyl germirene group, and other germirene groups substituted by C_{1-20} hydrocarbon substituents, groups bonded by nitrogen atoms, such as nitrene group, methyl nitrene group, phenyl nitrene group, and other nitrene groups substituted by C_{1-20} hydrocarbon substituents, groups bonded by oxygen atoms, such as oxyrene [transliteration] group, etc., groups bonded by sulfur atoms, such as sulfirene [transliteration] group, etc., groups bonded by selenium atoms, such as selenirene [transliteration] group, etc.

[0013]

The specific names of the bidentate chelating ligands that can be used as L in the present invention include chelating ligands coordinated to M by two phosphorus atoms, such as 1,1-

bis(diphenylphosphino)methane, 1,1-bis(dibutylphosphino)methane, 1,1-bis(dicyclohexylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(dibutylphosphino)ethane, 1,2-bis(dicyclohexylphosphino)ethane, 1,2-bis(phosphafluorenyl)ethane, 1,2-bis(diphenyl phosphoryl)ethane, 1,2-bis(diethyl phosphoranyl)ethane, 1,3-bis(diphenylphosphino)propane, 1,3-bis(dibutylphosphino)propane, 1,3-bis(dicyclohexylphosphino)propane, 1,3-bis(diphenyl phosphoryl)propane, 1,3-bis(phosphafluorenyl) propane 1,3-bis(diethyl phosphoranyl)propane, 1,2-bis(diphenylphosphino)benzene, 1,2-bis(dibutylphosphino)benzene, 1,2-bis(dicyclohexylphosphino)benzene, 1,2-bis(phosphofluorenyl)benzene, 1,2-bis(diphenyl phosphoryl)benzene, 1,2-bis(diethyl phosphoranyl)benzene, 2,2'-bis(dibutylphosphino)-6,6'-dimethyl-1,1'-biphenyl, 2,2'-bis(dicyclohexylphosphino)-1,1'-bisphenyl, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 2,2'-bis(dibutylphosphino)-1,1'-binaphthyl, 2,2'-bis(dicyclohexylphosphino)-1,1'-binaphthyl, 2,2'-bis(phosphafluorenyl)-1,1'-binaphthyl, 1,2-bis(diphenylphosphino)ferrocene, 1,2-bis(dibutylphosphino)ferrocene, 1,2-bis(dicyclohexylphosphino)ferrocene, 1,2-bis(phosphafluorenyl)ferrocene, 1,1'-bis(diphenylphosphino)ferrocene, 1,1'-bis(dibutylphosphino)ferrocene, 1,1'-bis(dicyclohexylphosphino)ferrocene, 1,1'-bis(phosphafluorenyl)ferrocene, [2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl][1,1'-binaphthalen-2,2'-diyl]phosphide, 1,2-bis[2-(2,4,6-tri-t-butylphenyl)phosphenomethyl]benzene, 1,2-bis[(2,4,6-tri-t-butylphenyl)phospheno]ethane, etc.; chelating ligands coordinated to M by two arsenic atoms, such as 1,1-bis(diphenylarsino)methane, 1,1-bis(dibutylarsino)methane, 1,1-bis(dicyclohexylarsino)methane, 1,2-bis(diphenylarsino)ethane, 1,2-bis(dibutylarsino)ethane, 1,2-bis(dicyclohexylarsino)ethane, 1,2-bis(arsafluorenyl)ethane, 1,3-bis(diphenylarsino)propane, 1,3-bis(dibutylarsino)propane, 1,3-bis(dicyclohexylarsino)propane, 1,3-bis(arsafluorenyl)propane, 1,2-bis(diphenylarsino)benzene, 1,2-bis(dibutylarsino)benzene, 1,2-bis(dicyclohexylarsino)benzene, 1,2-bis(arsafluorenyl)benzene, 2,2'-bis(dibutylarsino)-6,6'-dimethyl-1,1'-biphenyl, 2,2'-bis(dicyclohexylarsino)-1,1'-bisphenyl, 2,2'-bis(diphenylarsino)-1,1'-binaphthyl, 2,2'-bis(dibutylarsino)-1,1'-binaphthyl, 2,2'-bis(dicyclohexylarsino)-1,1'-binaphthyl, 2,2'-bis(arsafluorenyl)-1,1'-binaphthyl, 1,2-bis(diphenylarsino)ferrocene, 1,2-bis(dibutylarsino)ferrocene, 1,2-bis(dicyclohexylarsino)ferrocene, 1,2-bis(arsafluorenyl)ferrocene, 1,1'-bis(diphenylarsino)ferrocene, 1,1'-bis(dibutylarsino)ferrocene, 1,1'-bis(dicyclohexylarsino)ferrocene, 1,1'-bis(arsafluorenyl)ferrocene, etc.; chelate ligands coordinated to M by two antimony atoms, such as 1,1-bis(diphenyl stibino)methane, 1,1-bis(dibutyl stibino)methane, 1,1-bis(dicyclohexyl stibino)methane, 1,2-bis(diphenyl stibino)ethane, 1,2-bis(dibutyl stibino)ethane, 1,2-bis(dicyclohexyl stibino)ethane, 1,2-bis(stibafluorenyl)ethane, 1,3-bis(diphenyl stibino)propane, 1,3-bis(dibutyl stibino)propane, 1,3-

bis(dicyclohexyl stibino)propane, 1,3-bis(stibafluorenyl)propane, 1,2-bis(diphenyl stibino)benzene, 1,2-bis(dibutyl stibino)benzene, 1,2-bis(dicyclohexyl stibino)benzene, 1,2-bis(stibafluorenyl)benzene, 2,2'-bis(dibutyl stibino)-6,6'-dimethyl-1,1'-biphenyl, 2,2'-bis(dicyclohexyl stibino)-1,1'-bisphenyl, 2,2'-bis(diphenyl stibino)-1,1'-binaphthyl, 2,2'-bis(dibutyl stibino)-1,1'-binaphthyl, 2,2'-bis(dicyclohexyl stibino)-1,1'-binaphthyl, 2,2'-bis(stibafluorenyl)-1,1'-binaphthyl, 1,2-bis(diphenyl stibino)ferrocene, 1,2-bis(dibutyl stibino)ferrocene, 1,2-bis(dicyclohexyl stibino)ferrocene, 1,2-bis(stibafluorenyl)ferrocene, 1,1'-bis(diphenyl stibino)ferrocene, 1,1'-bis(dibutyl stibino)ferrocene, 1,1'-bis(dicyclohexyl stibino)ferrocene, 1,1'-bis(stibafluorenyl)ferrocene, etc.; chelate ligands coordinated to M by nitrogen atoms and phosphorus atoms, such as 1-N,N-dimethylamino-2-diphenylphosphino benzene, 1-N,N-dibutylamino-2-diphenylphosphino benzene, 1-N,N-dibutylamino-2-butylphosphino benzene, 1-N,N-dicyclohexylamino-2-diphenylphosphino benzene, 1-N,N-dicyclohexylamino-2-dicylohexylphosphino benzene, 1-N,N-dimethylaminomethyl-2-diphenylphosphino benzene, 1-carbazolyl-2-phosphafluorenylbenzene, 2-dimethylamino-2'-diphenylphosphino-6,6'-dimethyl-1,1'-biphenyl, 2-dibutylamino-2'-dibutylphosphino-6,6'-dimethyl-1,1'-biphenyl, 2-dicyclohexylamino-2'-dicyclohexylphosphino-6,6'-dimethyl-1,1'-biphenyl, 2-dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl, 2-dibutylamino-2'-diphenylphosphino-1,1'-binaphthyl, 2-dibutylamino-2'-dibutylphosphino-1,1'-binaphthyl, 2-dicyclohexylamino-2'-diphenylphosphino-1,1'-binaphthyl, 2-dicyclohexylamino-2'-dicyclohexylphosphino-1,1'-binaphthyl, 1-dimethylamino-2-diphenylphosphino ferrocene, 1-dibutylamino-2-dibutylphosphino ferrocene, 1-dicyclohexylamino-2-dicyclohexylphosphino ferrocene, 1-dimethylamino-1'-diphenylphosphino ferrocene, 1-diphenylamino-1'-diphenylphosphino ferrocene, 1-dibutylamino-1'-diphenylphosphino ferrocene, 1-dibutylamino-1'-dibutylphosphino ferrocene, 1-dicyclohexylamino-1'-dicyclohexylphosphino ferrocene, 1-(N-2,6-dimethylphenyl)imino-1-diphenylphosphino ethane, 1-(N-2,6-diisopropyl)imino-1-diphenylphosphino ethane, 1-(N-2,4,6-tri-t-butylphenyl)imino-1-diphenylphosphino ethane, 1-(N-2,6-dimethylphenyl)imino-2-diphenylphosphino ethane, 1-(N-2,6-dimethylphenyl)imino-2-dibutylphosphino ethane, 1-(N-2,6-dimethylphenyl)imino-2-dicyclohexylphosphino ethane, 1-(N-2,6-diisopropylphenyl)imino-2-diphenylphosphino ethane, 1-(N-2,6-diisopropylphenyl)imino-2-dibutylphosphino ethane, 1-(N-2,4,6-tri-t-butylphenyl)imino-2-diphenylphosphino ethane, 1-(N-2,6-dimethylphenyl)imino-3-diphenylphosphino propane, 1-(N-2,6-dimethylphenyl)imino-3-dibutylphosphino propane, 1-(N-2,6-dimethylphenyl)imino-3-dicyclohexylphosphino propane, 1-(N-2,6-diisopropylphenyl)imino-3-diphenylphosphino propane, 1-(N-2,6-diisopropylphenyl)imino-3-dibutylphosphino propane, 1-(N-2,6-diisopropylphenyl)imino-3-dicyclohexylphosphino propane, 1-(N-2,4,6-tri-t-butylphenyl)imino-3-diphenylphosphino propane, 1-(N-2,6-dimethylphenyl)methylimino-2-diphenylphosphino

benzene, 1-(N-2,6-dimethylphenyl)methylimino-2-dibutylphosphino benzene, 1-(N-2,6-dimethylphenyl)methylimino-2-dicyclohexylphosphino benzene, 1-(N-2,6-diisopropylphenyl)methylimino-2-diphenylphosphino benzene, 1-(N-2,6-diisopropylphenyl)methylimino-2-dibutylphosphino benzene, 1-(N-2,6-diisopropylphenyl)methylimino-2-dicyclohexylphosphino benzene, 1-(N-2,4,6-tri-t-butylphenyl)methylimino-2-diphenylphosphino benzene, etc.; chelate ligands coordinated to M by nitrogen atoms and arsenic atoms, such as 1-N,N-dimethylamino-2-diphenylarsino benzene, 1-N,N-dibutylamino-2-diphenylarsino benzene, 1-N,N-dibutylamino-2-butylarsino benzene, 1-N,N-dicyclohexylamino-2-diphenylarsino benzene, 1-N,N-dicyclohexylamino-2-dicylohexylarsino benzene, 1-carbazolyl-2-arsafluorenyl benzene, 2-dimethylamino-2'-diphenylarsino-6,6'-dimethyl-1,1'-biphenyl, 2-dibutylamino-2'-dibutylarsino-6,6'-dimethyl-1,1'-biphenyl, 2-dicyclohexylamino-2'-dicyclohexylarsino-6,6'-dimethyl-1,1'-biphenyl, 2-dimethylamino-2'-diphenylarsino-1,1'-binaphthyl, 2-dibutylamino-2'-diphenylarsino-1,1'-binaphthyl, 2-dibutylamino-2'-dibutylarsino-1,1'-binaphthyl, 2-dicyclohexylamino-2'-diphenylarsino-1,1'-binaphthyl, 2-dicyclohexylamino-2'-dicyclohexylarsino-1,1'-binaphthyl, 1-dimethylamino-2-diphenylarsino ferrocene, 1-dibutylamino-2-dibutylarsino ferrocene, 1-dicyclohexylamino-2-dicyclohexylarsino ferrocene, 1-dimethylamino-1'-diphenylarsino ferrocene, 1-diphenylamino-1'-diphenylarsino ferrocene, 1-dibutylamino-1'-dibutylarsino ferrocene, 1-dicyclohexylamino-1'-dicyclohexylarsino ferrocene, 1-(N-2,6-dimethylphenyl)imino-1-diphenylarsino ethane, 1-(N-2,6-diisopropyl)imino-1-diphenylarsino ethane, 1-(N-2,4,6-tri-t-butylphenyl)imino-1-diphenylarsino ethane, 1-(N-2,6-dimethylphenyl)imino-2-diphenylarsino ethane, 1-(N-2,6-dimethylphenyl)imino-2-dibutylarsino ethane, 1-(N-2,6-dimethylphenyl)imino-2-dicyclohexylarsino ethane, 1-(N-2,6-diisopropylphenyl)imino-2-diphenylarsino ethane, 1-(N-2,6-diisopropylphenyl)imino-2-dibutylarsino ethane, 1-(N-2,4,6-tri-t-butylphenyl)imino-2-diphenylarsino ethane, 1-(N-2,6-dimethylphenyl)imino-3-diphenylarsino propane, 1-(N-2,6-dimethylphenyl)imino-3-dibutylarsino propane, 1-(N-2,6-dimethylphenyl)imino-3-dicyclohexylarsino propane, 1-(N-2,6-diisopropylphenyl)imino-3-diphenylarsino propane, 1-(N-2,6-diisopropylphenyl)imino-3-dibutylarsino propane, 1-(N-2,6-diisopropylphenyl)imino-3-dicyclohexylarsino propane, 1-(N-2,4,6-tri-t-butylphenyl)imino-3-diphenylarsino propane, 1-(N-2,6-dimethylphenyl)methylimino-2-diphenylarsino benzene, 1-(N-2,6-dimethylphenyl)methylimino-2-dibutylarsino benzene, 1-(N-2,6-dimethylphenyl)methylimino-2-dicyclohexylarsino benzene, 1-(N-2,6-diisopropylphenyl)methylimino-2-diphenylarsino benzene, 1-(N-2,6-diisopropylphenyl)methylimino-2-dibutylarsino benzene, 1-(N-2,6-diisopropylphenyl)methylimino-2-dicyclohexylarsino benzene, 1-(N-2,4,6-tri-t-butylphenyl)methylimino-2-diphenylarsino benzene, etc.

[0014]

X includes a hydrogen atom and the monovalent ligands selected from the groups bonded with M by elements from groups 14-17 of the periodic table. Examples of the groups bonded with M by elements from groups 14-17 of the periodic table include groups bonded by elements from group 14 of the periodic table, such as methyl group, ethyl group, propyl group, butyl group, cyclohexyl group, and other C_{1-20} alkyl groups, benzyl group, and other C_{7-20} arylalkyl groups, phenyl group, tolyl group, and other C_{6-20} alkylaryl groups, trimethylsilyl group, tributylsilyl group, triphenylsilyl group, and other silyl groups substituted by C_{1-20} hydrocarbon groups; groups bonded by an element selected from group 15 of the periodic table, such as amido group, dimethylamido group, dibutylamido group, diphenylamido group, and other amido groups substituted by C_{1-20} hydrocarbon substituents; groups bonded by means of an element selected from group 16 of the periodic table, such as hydroxyl group, methoxy group, ethoxy group, butoxy group, and other alkoxy groups substituted by C_{1-20} hydrocarbon substituents, phenoxy group, tolyloxy group, and other C_{6-20} alkylaryloxy groups, benzyloxy group, and other C_{7-20} arylalkyloxy groups, thiohydroxy group, thiomethoxy group, thioethoxy group, thiobutoxy group, and other C_{1-20} thioalkoxy groups, thiophenoxy group, thiotolyloxy group, and other C_{6-20} thioalkylaryloxy groups, thiobenzyloxy group, and other C_{7-20} thioarylalkyloxy group, etc.; groups bonded by means of element selected from group 17 of the periodic table, such as a fluorine atom, chlorine atom, bromine atom, and iodine atom, or preferably chlorine atom and bromine atom. The two Xs may be identical to each other or different from each other, and they may be connected to each other by a covalent bond.

[0015]

M represents a transition metal element selected from elements from group 10 of the periodic table, or preferably Ni and Pd, or more preferably Ni. Specific names of the compounds that can be used as (I) in the present invention include the following types: compound having chelate ligands coordinated to M by two phosphorus atoms, such as 1,1-bis(diphenylphosphino)methane nickel dichloride, 1,1-bis(dibutylphosphino)methane nickel dichloride, 1,1-bis(dicyclohexylphosphino)methane nickel dichloride, 1,2-bis(diphenylphosphino)ethane nickel dichloride, 1,2-bis(diphenylphosphino)ethane nickel dimethyl, 1,2-bis(diphenylphosphino) ethane palladium dichloride, 1,2-bis(diphenylphosphino)ethane platinum dichloride, 1,2-bis(dibutylphosphino)ethane palladium dichloride, 1,2-bis(dibutylphosphino)ethane palladium dichloride, 1,2-bis(dicyclohexylphosphino)ethane nickel dichloride, 1,2-bis(phosphafluorenyl)ethane nickel dichloride, 1,2-bis(diphenyl phosphoryl)ethane nickel dichloride, 1,2-bis(diethyl

phosphoranyl)ethane nickel dichloride, 1,3-bis(diphenylphosphino)propane nickel dichloride, 1,3-bis(dibutylphosphino)propane nickel dichloride, 1,3-bis(dicyclohexylphosphino)propane nickel dichloride, 1,3-bis(phosphafluorenyl)propane nickel dichloride, 1,3-bis(diphenyl phosphoryl)propane nickel dichloride, 1,3-bis(diethyl phosphoranyl)propane nickel dichloride, 1,2-bis(diphenylphosphino)benzene nickel dichloride, 1,2-bis(diphenylphosphino)benzene nickel dimethyl, 1,2-bis(diphenylphosphino)benzene palladium dichloride, 1,2-bis(dibutylphosphino)benzene nickel dichloride, 1,2-bis(dibutylphosphino)benzene palladium dichloride, 1,2-bis(dicyclohexylphosphino)benzene nickel dichloride, 1,2-bis(phosphafluorenyl)benzene nickel dichloride, 1,2-bis(diphenyl phosphoryl)benzene nickel dichloride, 1,2-bis(diethyl phosphoranyl)benzene nickel dichloride, 2,2'-bis(dibutylphosphino)-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2,2'-bis(dicyclohexylphosphino)-1,1'-bisphenyl nickel dichloride, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(dibutylphosphino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(dibutylphosphino)-1,1'-binaphthyl palladium dichloride, 2,2'-bis(dibutylphosphino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(dicyclohexylphosphino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(phosphafluorenyl)-1,1'-binaphthyl nickel dichloride, 1,2-bis(diphenylphosphino)ferrocene nickel dichloride, 1,2-bis(dibutylphosphino)ferrocene, 1,2-bis(dicyclohexylphosphino)ferrocene nickel dichloride, 1,2-bis(phosphafluorenyl)ferrocene nickel dichloride, 1,1'-bis(diphenylphosphino)ferrocene nickel dichloride, 1,1'-bis(dicyclohexylphosphino)ferrocene nickel dichloride, 1,1'-bis(dicyclohexylphosphino)ferrocene nickel dimethyl, 1,1'-bis(dicyclohexylphosphino)ferrocene palladium dichloride, 1,1'-bis(dibutylphosphino)ferrocene nickel dichloride, 1,1'-bis(dicyclohexylphosphino)ferrocene nickel dichloride, 1,1'-bis(phosphafluorenyl)ferrocene nickel dichloride, [2-(diphenylphosphino)-1,1'-binaphthalene-2'-yl][1,1'-binaphthalene-2,2'-diyl]phosphide nickel dichloride, [2-(diphenylphosphino)-1,1'-binaphthalene-2'-yl][1,1'-binaphthalene-2,2'-diyl]phosphide palladium dichloride, 1,2-bis[2-(2,4,6-tri-t-butylphenyl)phosphenomethyl]benzene nickel dichloride, 1,2-bis[2-(2,4,6-tri-t-butylphenyl)phosphenomethyl]benzene palladium dichloride, etc.; [compounds having] chelate ligands coordinated to M by two arsenic atoms, such as 1,1-bis(diphenylarsino)methane nickel dichloride, 1,1-bis(dibutylarsino)methane nickel dichloride, 1,1-bis(dicyclohexylarsino)methane nickel dichloride, 1,2-bis(diphenylarsino)ethane nickel dichloride, 1,2-bis(diphenylarsino)ethane palladium dichloride, 1,2-bis(dibutylarsino)ethane nickel dichloride, 1,2-bis(dicyclohexylarsino)ethane, 1,2-bis(arsafluorenyl)ethane nickel dichloride, 1,3-bis(diphenylarsino)propane nickel dichloride, 1,3-bis(dibutylarsino)propane nickel dichloride, 1,3-bis(dicyclohexylarsino)propane, 1,3-bis(arsafluorenyl)propane nickel dichloride, 1,2-bis(diphenylarsino)benzene mechanical displacement, 1,2-bis(diphenylarsino)benzene palladium dichloride, 1,2-bis(dibutylarsino)benzene nickel dichloride, 1,2-bis(dicyclohexylarsino)benzene

nickel dichloride, 1,2-bis(arsafluorenyl)benzene nickel dichloride, 2,2'-bis(dibutylarsino)-6,6'-dimethyl-1,1'-biphenyl, 2,2'-bis(dicyclohexylarsino)-1,1'-bisphenyl nickel dichloride, 2,2'-bis(diphenylarsino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(diphenylarsino)-1,1'-binaphthyl palladium dichloride, 2,2'-bis(dibutylarsino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(dicyclohexylarsino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(arsafluorenyl)-1,1'-binaphthyl nickel dichloride, 1,2-bis(diphenylarsino)ferrocene nickel dichloride, 1,2-bis(dibutylarsino)ferrocene nickel dichloride, 1,2-bis(dicyclohexylarsino)ferrocene nickel dichloride, 1,2-bis(arsafluorenyl)ferrocene nickel dichloride, 1,1'-bis(diphenylarsino)ferrocene nickel dichloride, 1,1'-bis(dibutylarsino)ferrocene nickel dichloride, 1,1'-bis(dicyclohexylarsino)ferrocene nickel dichloride, 1,1'-bis(arsafluorenyl)ferrocene nickel dichloride, etc.; compounds having chelate ligands coordinated to M by two antimony atoms, such as 1,1-bis(diphenyl stibino)methane nickel dichloride, 1,1-bis(dibutyl stibino)methane nickel dichloride, 1,1-bis(dicyclohexyl stibino)methane nickel dichloride, 1,2-bis(diphenyl stibino)ethane nickel dichloride, 1,2-bis(dibutyl stibino)ethane nickel dichloride, 1,2-bis(dicyclohexyl stibino)ethane nickel dichloride, 1,2-bis(stibafluorenyl)ethane nickel dichloride, 1,3-bis(diphenyl stibino)propane nickel dichloride, 1,3-bis(dibutyl stibino)propane nickel dichloride, 1,3-bis(dicyclohexyl stibino)propane nickel dichloride, 1,3-bis(stibafluorenyl)propane nickel dichloride, 1,2-bis(diphenyl stibino)benzene nickel dichloride, 1,2-bis(dibutyl stibino)benzene nickel dichloride, 1,2-bis(dicyclohexyl stibino)benzene nickel dichloride, 1,2-bis(stibafluorenyl)benzene nickel dichloride, 2,2'-bis(dibutyl stibino)-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2,2'-bis(dicyclohexyl stibino)-1,1'-bisphenyl nickel dichloride, 2,2'-bis(diphenyl stibino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(dibutyl stibino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(dicyclohexyl stibino)-1,1'-binaphthyl nickel dichloride, 2,2'-bis(stibafluorenyl)-1,1'-binaphthyl nickel dichloride, 1,2-bis(diphenyl stibino)ferrocene nickel dichloride, 1,2-bis(dibutyl stibino)ferrocene nickel dichloride, 1,2-bis(dicyclohexyl stibino)ferrocene nickel dichloride, 1,2-bis(stibafluorenyl)ferrocene nickel dichloride, 1,1'-bis(diphenyl stibino)ferrocene nickel dichloride, 1,1'-bis(dibutyl stibino)ferrocene nickel dichloride, 1,1'-bis(dicyclohexyl stibino)ferrocene nickel dichloride, 1,1'-bis(stibafluorenyl)ferrocene nickel dichloride, etc.; compounds having chelate ligands coordinated to M by nitrogen atoms and phosphorus atoms, such as 1-N,N-dimethylamino-2-diphenylphosphino benzene nickel dichloride, 1-N,N-dimethylamino-2-diphenylphosphino benzene palladium dichloride, 1-N,N-dibutylamino-2-diphenylphosphino benzene nickel dichloride, 1-N,N-dibutylamino-2-butylphosphino benzene nickel dichloride, 1-N,N-dibutylamino-2-butylphosphino benzene palladium dichloride, 1-N,N-dicyclohexylamino-2-diphenylphosphino benzene nickel dichloride, 1-N,N-dicyclohexylamino-2-dicyclohexylphosphino benzene nickel dichloride, 1-N,N-dimethylaminomethyl-2-

diphenylphosphino benzene nickel dichloride, 1-carbazolyl-2-phosphafluorenyl benzene nickel dichloride, 2-dimethylamino-2'-diphenylphosphino-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2-dibutylamino-2'-dibutylphosphino-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2-dicyclohexylamino-2'-dicyclohexylphosphino-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2-dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl nickel dichloride, 2-dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl palladium dichloride, 2-dibutylamino-2'-diphenylphosphino-1,1'-binaphthyl nickel dichloride, 2-dibutylamino-2'-dibutylphosphino-1,1'-binaphthyl nickel dichloride, 2-dicyclohexylamino-2'-diphenylphosphino-1,1'-binaphthyl nickel dichloride, 2-dicyclohexylamino-2'-dicyclohexylphosphino-1,1'-binaphthyl nickel dichloride, 1-dimethylamino-2-diphenylphosphino ferrocene nickel dichloride, 1-dibutylamino-2-dibutylphosphino ferrocene nickel dichloride, 1-dicyclohexylamino-2-dicyclohexylphosphino ferrocene nickel dichloride, 1-dimethylamino-1'-diphenylphosphino ferrocene nickel dichloride, 1-diphenylamino-1'-diphenylphosphino ferrocene nickel dichloride, 1-dibutylamino-1'-diphenylphosphino ferrocene nickel dichloride, 1-dibutylamino-1'-dibutylphosphino ferrocene nickel dichloride, 1-dicyclohexylamino-1'-dicyclohexylphosphino ferrocene nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-1-diphenylphosphino ethane nickel dichloride, 1-(N-2,6-diisopropyl)imino-1-diphenylphosphino ethane nickel dichloride, 1-(N-2,6-diisopropyl)imino-1-diphenylphosphino ethane palladium dichloride, 1-(N-2,4,6-tri-t-butylphenyl)imino-1-diphenylphosphino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-2-diphenylphosphino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-2-dibutylphosphino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-2-dicyclohexylphosphino ethane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-2-diphenylphosphino ethane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-2-dibutylphosphino ethane nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)imino-2-diphenylphosphino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-3-diphenylphosphino propane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-3-dibutylphosphino propane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-3-dicyclohexylphosphino propane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-3-diphenylphosphino propane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-3-dibutylphosphino propane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-3-dicyclohexylphosphino propane nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)imino-3-diphenylphosphino propane nickel dichloride, 1-(N-2,6-dimethylphenyl)methylimino-2-diphenylphosphino benzene nickel dichloride, 1-(N-2,6-dimethylphenyl)methylimino-2-dibutylphosphino benzene nickel dichloride, 1-(N-2,6-dimethylphenyl)methylimino-2-dicyclohexylphosphino benzene nickel dichloride, 1-(N-2,6-diisopropylphenyl)methylimino-2-diphenylphosphino benzene nickel dichloride, 1-(N-2,6-diisopropylphenyl)methylimino-2-diphenylphosphino benzene palladium dichloride, 1-(N-2,6-

diisopropylphenyl)methylimino-2-dibutylphosphino benzene nickel dichloride, 1-(N-2,6-diisopropylphenyl)methylimino-2-dicyclohexylphosphino benzene nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)methylimino-2-diphenylphosphino benzene nickel dichloride, etc.; compounds having chelate ligands coordinated to M by nitrogen atoms and arsenic atoms, such as 1-N,N-dimethylamino-2-diphenylarsino benzene nickel dichloride, 1-N,N-dibutylamino-2-diphenylarsino benzene nickel dichloride, 1-N,N-dibutylamino-2-butylarsino benzene nickel dichloride, 1-N,N-dicyclohexylamino-2-diphenylarsino benzene nickel dichloride, 1-N,N-dicyclohexylamino-2-dicyclohexylarsino benzene nickel dichloride, 1-carbazolyl-2-arsafluorenyl benzene nickel dichloride, 2-dimethylamino-2'-diphenylarsino-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2-dibutylamino-2'-dibutylarsino-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2-dicyclohexylamino-2'-dicyclohexylarsino-6,6'-dimethyl-1,1'-biphenyl nickel dichloride, 2-dimethylamino-2'-diphenylarsino-1,1'-binaphthyl nickel dichloride, 2-dibutylamino-2'-diphenylarsino-1,1'-binaphthyl nickel dichloride, 2-dibutylamino-2'-dibutylarsino-1,1'-binaphthyl nickel dichloride, 2-dicyclohexylamino-2'-diphenylarsino-1,1'-binaphthyl nickel dichloride, 2-dicyclohexylamino-2'-dicyclohexylarsino-1,1'-binaphthyl nickel dichloride, 1-dimethylamino-2-diphenylarsino ferrocene nickel dichloride, 1-dibutylamino-2-dibutylarsino ferrocene nickel dichloride, 1-dicyclohexylamino-2-dicyclohexylarsino ferrocene nickel dichloride, 1-dimethylamino-1'-diphenylarsino ferrocene nickel dichloride, 1-diphenylamino-1'-diphenylarsino ferrocene nickel dichloride, 1-dibutylamino-1'-dibutylarsino ferrocene nickel dichloride, 1-dicyclohexylamino-1'-dicyclohexylarsino ferrocene nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-1-diphenylarsino ethane nickel dichloride, 1-(N-2,6-diisopropyl)imino-1-diphenylarsino ethane nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)imino-1-diphenylarsino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-2-diphenylarsino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-2-dibutylarsino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-2-dicyclohexylarsino ethane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-2-diphenylarsino ethane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-2-dibutylarsino ethane nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)imino-2-diphenylarsino ethane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-3-diphenylarsino propane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-3-dibutylarsino propane nickel dichloride, 1-(N-2,6-dimethylphenyl)imino-3-dicyclohexylarsino propane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-3-diphenylarsino propane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-3-dibutylarsino propane nickel dichloride, 1-(N-2,6-diisopropylphenyl)imino-3-dicyclohexylarsino propane nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)imino-3-diphenylarsino propane nickel dichloride, 1-(N-2,6-dimethylphenyl)methylimino-2-diphenylarsino benzene nickel dichloride, 1-(N-2,6-dimethylphenyl)methylimino-2-dibutylarsino benzene nickel dichloride, 1-(N-2,6-

dimethylphenyl)methylimino-2-dicyclohexylarsino benzene nickel dichloride nickel dichloride, 1-(N-2,6-diisopropylphenyl)methylimino-2-diphenylarsino benzene nickel dichloride, 1-(N-2,6-diisopropylphenyl)methylimino-2-dibutylarsino benzene nickel dichloride, 1-(N-2,6-diisopropylphenyl)methylimino-2-dicyclohexylarsino benzene nickel dichloride, 1-(N-2,4,6-tri-t-butylphenyl)methylimino-2-diphenylarsino benzene nickel dichloride, etc.

[0016]

In the polymerization operation, it is preferred that an acidic substance be used as an assisting catalyst for the principal catalyst. As far as the acidic substance is concerned, one may use any of inorganic substances or organic substances in any form of gas, liquid, and solid, as long as it has acidic property. Especially preferable are organic aluminum compounds or ion pair type compounds having non-coordinated anions. Specific names of the organic aluminum compounds for use in the present invention include methyl aluminoxane, ethyl aluminoxane, butyl aluminoxane, methylbutyl aluminoxane, and other aluminoxanes, trimethylaluminum, trimethylaluminum, triisobutylaluminum, and other trialkylaluminums, triphenylaluminum, tris(pentafluorophenyl)aluminum, and other triarylaluminums, methylaluminum dichloride, dimethylaluminum chloride, diethylaluminum chloride, isobutylaluminum sesquichloride, and other halogenated alkylaluminums, etc.

[0017]

The ion pair type compounds having non-coordinated anions are compounds represented by the following general formula (V):

$$[C]^{+}[A]^{-} \qquad (V)$$

Here, [C]+ represents proton, carbenium ion, tropylium ion, ammonium ion, phosphonium ion, oxonium ion, sulfonium ion, ferrocenium ion, Ag(I) cation, etc. $[A]^{-}$ represents tetraphenyl borate, tetrakis(pentafluorophenyl) borate, tetrakis(bistrifluoromethylphenyl) borate, tetrafluoroborate, hexafluorophosphate, perchloric anion, p-toluenesulfonic anion, and other non-coordinated anions.

[0018]

Examples of the ion pair type compounds used as the assisting catalyst include dimethyl anilinium tetraphenyl borate, dimethyl anilinium tetrakis(pentafluorophenyl) borate, dimethyl anilinium tetrakis(bistrifluoromethyl) phenyl borate, triphenyl carbenium tetraphenyl borate, triphenyl carbenium tetrakis(pentafluorophenyl) borate, triphenyl carbenium tetrakis(bistrifluoromethyl)phenyl borate, ferrocenium tetraphenyl borate, ferrocenium

tetrakis(pentafluorophenyl) borate, dimethyl ferrocenium tetrakis(pentafluorophenyl) borate, Ag(I) tetraphenyl borate, Ag(I) tetrakis(pentafluorophenyl) borate, etc.

[0019]

There is no specific restriction on the polymerization method for polymerization of olefin. One may use any of the well-known suspension polymerization method, solution polymerization method, or other liquid-phase polymerization method, or gas-phase polymerization method. Examples of the solvents that can be used as the liquid-phase polymerization method include toluene, hexane, and other inactive hydrocarbons. Also, one may use propylene or other olefin for polymerization itself. Polymerization temperature is in the range of -50 to 250°C, and the polymerization pressure is selected in the range of 1-200 kgf/cm^2. As far as the polymerization system is concerned, one may use any of the batch system, semi-continuous system, and continuous system. Also, it is possible to perform the operation by dividing it into two or more stages with different polymerization conditions. In the polymerization operation, the catalysts of the present invention may be used either alone or as a mixture. In addition, it may be mixed with the compounds of transition metal elements from group 4 of the periodic table or other olefin polymerization catalysts for use.

[0020]

Examples of olefins that can be used in the polymerization or copolymerization include α-olefins, such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, etc. Also, the following compounds may also be used in the polymerization or copolymerization: styrene, p-methylstyrene, and other terminal vinyl compounds having aromatic as substituents, vinyl silane, and other terminal vinyl compounds having silyl groups as substituents, vinyl norbornene, vinyl cyclohexane, and other terminal vinyl compounds having cyclic hydrocarbons as substituents, cyclopentene, cyclohexane, cyclooctene, 1,3-cyclohexadiene, and other cyclic olefins, 1,5-hexadiene, 1,4-hexadiene, 1,4-cyclohexadiene, cyclooctadiene, and other non-conjugated dienes, etc.

[0021]

Embodiments of the invention

In the following, an explanation will be given regarding the present invention with reference to application examples. However, the present invention is not limited to the following application examples.

[0022]

Application Example 1

(Synthesis of catalyst)

According to the method described in Chem, Lett., 1980, p. 767, 1,1'-bis(diphenylphosphino)ferrocene nickel dichloride was prepared. That is, in a 1000-mL 3-neck flask with nitrogen flow, 5.54 g (10 mmol) of diphenylphosphino ferrocene (product of Kanto Kagaku K.K.) and 400 mL of 2-propanol were added, and the mixture was agitated while heated. Here, a solution prepared by dissolving 3.70 g (10 mmol) of nickel dichloride hexahydrate in 300 mL of 2:1 (ratio by volume) of 2-propanol and methanol was added into the flask. After 2 h of heating with reflux, the generated precipitate was filtered out and dried, forming 5.81 g of 1,1'-bis(diphenylphosphino) ferrocene nickel dichloride as a green solid substance.

(Polymerization)

In a well-dried 1.5-L autoclave in nitrogen gas flow, 600 mL of toluene, 4 mmol (Al-atom equivalent) of methylaluminoxane, and 20 μmol of 1,1'-bis(diphenylphosphino) ferrocene nickel dichloride were added, and polymerization was performed for ethylene under an ethylene pressure of 10 kgf/cm^2 at 40°C for 1 h. As a result, 2.5 g of polymer were obtained (with polymer activity of 1.3 x 10^5 gPE/molNihr). For the obtained polymer, GPC (150-CV model, product of Waters Corp.) was performed to measure the molecular weight and molecular weight distribution. It was found that Mw = 8.6x10^5, Mw/Mn = 2.4. Also, NMR (JNM-A400 model, product of NEC) was performed to measure the ^{13}CNMR spectrum of the obtained polymer, and according to the method described in the following reference: Macromolecules, 1984, Vol. 17, p. 1756, the number of the branches for 1000 C was determined. As a result, it was found that the number of branches are as follows: methyl branches: 15; ethyl branches: 1; propyl branches: 0; butyl branches: 2; pentyl branches: 0; C_6 or longer chain branches: 6.

[0023]

Application Example 2

An experiment was performed in the same way as in Application Example 1, except that instead of 4 mmol of methyl aluminoxane, 0.2 mmol of diethylaluminum chloride was used. As a result, 2.0 g of polymer were obtained (with polymer activity of 1.0 x 10^5 gPE/molNihr). For the obtained polymer, GPC was performed to measure the molecular weight and molecular weight distribution. It was found that Mw = 8.8x10^5, M1/Mn = 2.3. Also, ^{13}CNMR spectrum was measured for the obtained polymer, and the number of branches for 1000 C of the polymer are as follows: methyl branches: 13; ethyl branches: 1; propyl branches: 0; butyl branches: 1; pentyl branches: 0; C6 or longer chain branches: 5.

[0024]

Application Example 3

(Synthesis of catalyst)

First, according to the method described in J. Chem Soc., 1965, p. 5210, 1-N,N-dimethylamino-2-diphenylphosphino benzene was prepared. That is, in a well-dried 200-mL 3-neck flask with nitrogen gas flow, 25 mL (25 mmol) of 1 mol/L ether solution of n-butyllithium were added, and the flask was cooled to -20°C and the content was agitated. Here, a solution prepared by dissolving 5.0 g (25 mmol) of o-bromo-N,N-dimethylaniline in 50 mL of ether was added dropwise over 1 h. While the solution was agitated, it was once heated to room temperature over 1 h, and was then cooled again to -40°C. Then, a solution prepared by dissolving 4.4 mL (24 mmol) of chlorodiphenylphosphine in 50 mL of ether was added dropwise over 1.5 h or longer time. While the solution was agitated, it was once heated to the room temperature for 1 h, and was then cooled in an ice bath. Then, 1N hydrochloric acid was added, and the water phase was neutralized in sodium hydroxide, and the product was extracted by ether. The ether phase was subjected to vacuum drying, and the obtained residue was recrystallized from ether, forming 3.7 g of 1-N,N-dimethylamino-2-diphenylphosphino benzene as a white solid substance.

[0025]

Then, according to the method described in J. Chem Soc., 1968, p. 205, 1-N,N-dimethylamino-2-diphenylphosphino benzene nickel dichloride was prepared. That is, in a 1000-mL 3-neck flask with nitrogen gas flow, 3.7 g (10 mmol) of nickel dichloride hexahydrate and 400 mL of n-butanol were added, and the content was agitated while heated. Here, a solution prepared by dissolving 3.1 g of said prepared 1-N,N-dimethylamino-2-diphenylphosphino benzene in 300 mL of heated n-butanol was added. After the contents were heated and agitated for 1 h, and generated precipitate was filtered out and dried, forming 4.6 g of 1-N,N-dimethylamino-2-diphenylphosphino benzene nickel dichloride as a brown solid substance.

(Polymerization)

Polymerization was performed in the same way as in Application Example 1, except that instead of 1,1'-bis(diphenylphosphino)ferrocene nickel dichloride, 1-N,N-dimethylamino-2-diphenylphosphino benzene nickel dichloride was used. As a result, 8.5 g of polymer was obtained (with polymer activity of 4.3×10^5 gPE/molNihr). For the obtained polymer, GPC was performed to measure the molecular weight and molecular weight distribution. It was found that $Mw = 9.2 \times 10^5$, $Mw/Mn = 2.6$. Also, ^{13}CNMR spectrum was measured for the obtained

polymer, and the number of branches for 1000 C of the polymer are as follows: methyl branches: 18; ethyl branches: 1; propyl branches: 0; butyl branches: 2; pentyl branches: 0; C_6 or longer chain branches: 6.

[0026]

Comparative Example 1

The experiment was performed in the same way as in Application Example 1, except that instead of 1,1'-bis(diphenylphosphino)ferrocene nickel dichloride, (triphenylphosphine) (o-oxyphenyl diphenylphosphino)phenyl nickel was used. As a result, 0.4 g of polymer was obtained (with polymer activity of 2.0×10^4 gPE/molNihr). For the obtained polymer, GPC was performed to measure the molecular weight and molecular weight distribution. It was found that $Mw = 1.1 \times 10^4$, Mw/Mn = 2.3. Also, ^{13}CNMR spectrum was measured for the obtained polymer, and the number of branches for 1000 C of the polymer are as follows: methyl branches: 6; ethyl branches: 0; propyl branches: 0; butyl branches: 2; pentyl branches: 0; C_6 or longer chain branches: 2.

[0027]

Effect of the invention

According to the method of the present invention for polymerization of olefin, compared with the conventional method using a transition metal compound of elements from group 10 of the periodic table, it is possible to obtain polyolefin with a high molecular weight and having a branched structure at a high yield.

Brief description of the figures

Figure 1 is a flow chart illustrating preparation of the catalyst according to the present invention.

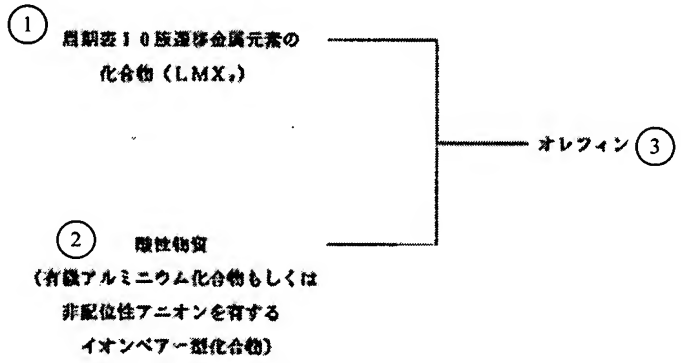

Figure 1

Key: 1 Compound of transition metal element from group 10 of the periodic table (LMX_2)

2 Acidic substance (organic aluminum compound or ion pair type compound having non-coordinated anions)

3 Olefin